EMISSION SPECTRUM OF MgCl: A NEW DOUBLET SYSTEM

V. SATYANARAYANA RAO AND P. TIRUVENGANNA RAO

SPECTROSCOPIC LABORATORIES, DEPARTMENT OF PHYSICS, ANDHRA UNIVERSITY, WALTAIR

(*Received, July 5, 1963, resubmitted, December 23, 1963*)

Plate IX

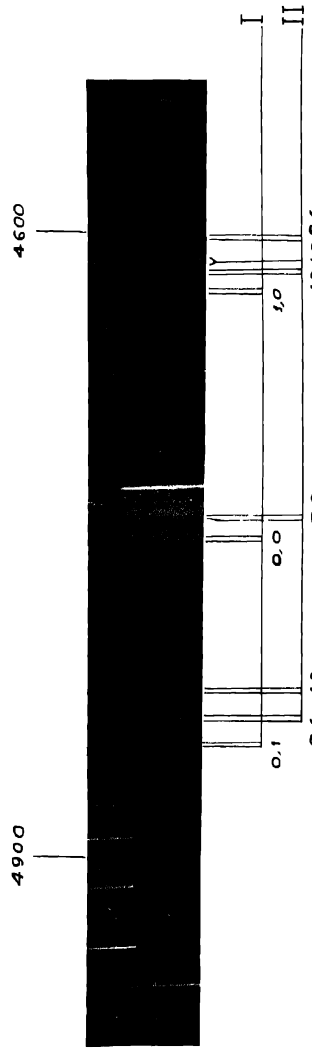
ABSTRACT A new doublet system of bands attributed to MgCl molecule has been observed in the visible region λ5000-λ4550 in the high frequency discharge. From the vibrational analysis of the system it is concluded that the lower state of this system is same as the first excited $A\,^2\Pi$ state of MgCl with a doublet separation of 55 cm^{-1}. The approximate vibrational constants of the upper state are estimated as $\omega_e' = 563\ cm^{-1}$ and $\omega_e' x_e' = 5.5\ cm^{-1}$.

The electronic structures of the ground and excited states of MgCl are discussed in relation to those of BeF and MgF.

INTRODUCTION

The band spectrum of MgCl was investigated by Querbach (1930), Parker (1935), Morgan (1936) and Known to consist of only one discrete band system in the region λ3600-λ3950 Å. According to Morgan (1936) this system is a doublet system arising from a transition of the type $^2\Pi - {}^2\Sigma$ analogus to the well known $^2\Pi_i - X^2\Sigma$ system of BeF and MgF. The electronic structures of the diatomic halides of Berryllium and Magnesium are expected to be similar in their ground state as they contain the same number of outer valence electrons. By analogy with BeF and MgF one might expect that the ground state of these molecules is a $^2\Sigma$ state. The transition from the first excited $A^2\Pi$ state to the 'X' ground state gives rise to a strong system of bands degraded to violet in the spectra of each of the molecules MgF, MgCl and MgBr. In addition to this main system, transitions from two excited states $B^2\Sigma$ and $C^2\Sigma$ to the common $X^2\Sigma$ ground state have been identified by early workers. In the case of MgCl, fragments of four band systems are given at 12700 cm^{-1} by Querbach (1930), at 25900 cm^{-1} by Parker (1935), at 37060 cm^{-1} and 40850 cm^{-1} by Harrington (1942) in absorption. However no detailed analysis of any of these systems appears to have been reported so far.

During the course of an investigation on the emission spectrum of diatomic MgCl excited in high frequency discharge the authors have obtained a new system of bands in the region λ5000 – λ4550, in addition to the well known $A^2\Pi - X^2\Sigma$ system. The results of the vibrational analyses of the systems reported in this paper definitely indicate that the bands are to be attributed to diatomic MgCl.



MgCl Bands in the visible region New Doublet System.
I = Band Heads of Sub-System I.
II = Band heads of sub-System II.

The electronic structures of MgF and MgCl in their ground and excited states are also discussed in this paper

EXPERIMENTAL

The spectrum of MgCl was excited in high frequency discharge from a 500 Watt oscillator working at a frequency of 30 to 40 Mc/*S*., using an anhydrous specpure *P* sample of $MgCl_2$ in a conventional discharge tube. The discharge which was bright green in colour was photographed under low pressure vapour conditions using 3 prism Glass Littrow Spectrograph having a dispersion 7 Å/mm at 4000 Å. Exposures of 5 minutes duration were found sufficient for obtaining good spectrograms using Agfa Isopan superspecial plates For preliminary survey spectra were also photographed on Fuess and Medium Quartz instruments in the visible and ultra violet regions Measurements of band heads were made on Hilger comparator using Iron arc lines as standards and are accurate upto 2 cm^{-1}.

RESULTS AND ANALYSIS

In addition to the well known $A^2\Pi - X^2\Sigma$ system in the spectrum of MgCl a new system of bands was observed in the region $\lambda 5000 - \lambda 4550$ as can be seen in Fig (I) This system consists of three marked sequences of bands degraded towards the violet The wave number intensity and other data of the bands are given in table (I) The measurements of the band heads do not agree with the bands of any of the previously known systems of MgO, MgF, MgBr or with any of the commonly occurring impurity bands

TABLE I

Wave number in cm^{-1}	Intensity	Classification v′ v″	Band head
20641 4	4	0,1	${}^0P_{12}$
20650 2	2	0,1	P_2
20696 4	3	0,1	P_1
20708 0	5	0,1	Q_1
20761 8	2	1,2	P_1
20772 1	4	1,2	Q_1
21128 2	5	0,0	${}^0P_{12}$
21136 8	10	0,0	P_2
21183 3	5	0,0	P_1
21191 9	10	0,0	Q_1
21679 3	2	0,0	${}^0P_{12}$
21687 8	5	1,0	P_{-1}
21729 9	1	1,0	Pi_1
21735 9	3	1,0	P_1
21739 8	3	1,0	Qi_1
21745 4	6	1,0	Q_1
21798 3	1	2,1	P_1
21800 4	2	2,1	Q_1

The analysis of the system was greatly facilitated by identification of the strongest group as $\Delta v = 0$ sequence. The two weaker sequences $\Delta v = -1$ and -2 were easily identified on the longer wave length side and $\Delta v = +1$ sequence on the shorter wave length side of these Of these the $\Delta v = -2$ sequence is too weak for measurement The observed double double headed nature of the bands in $\Delta v = 0$ sequence immediately suggested the possibility that the system arises from a $^2\Sigma - {}^2\Pi$ $^2\Sigma$ or $^2\Pi - {}^2\Sigma$ transition From the structure of $^2\Sigma - {}^2\Pi$ transition we expect the following head forming branches $^pP_{12}$, $P_2 + pQ_{12}$ P_1 and $Q_1 + {}^qP_{21}$ for bands degraded towards the violet Thus each band with a particular value of v' and v'' is expected to consist of the above four heads. The intensities of the Q heads is

TABLE II

Vibrational analysis of the sub-system I of MgCl Bands

v′	v″ = 0		v″ = 1
0	21128 2	486 8	20641 4
	21136 8	486 6	20650 2
	551 1		
	551 0		
1	21679 3		
	21687 8		

TABLE III

Vibrational analysis of the sub-system II of MgCl Bands

v′	v″ = 0		1	2
0	21183 3	486 9	20696 4	
	21191 9	483 9	20708 0	
	552 6			
	553 5			
1	21735.9			20761.8
	21745 4			20772.1
2			21790 8	
			21800 4	

expected to be twice as strong as the P heads The detailed classifications of the band heads are given in columns 3 and 4 of Table I The observed intensities of band heads given in column (2) are in accordance with those expected for $^2\Sigma - ^2\pi$ transition The vibrational analyses of the two sub-systems are displayed in Tables II and III The first ΔG_v interval of the lower state of the two sub-systems agrees very well with the first vibrational quantum of $A^2\Pi$ state of MgCl. Further the corresponding bands of the two systems are separated by wave number interval of about 55 cm $^{-1}$ which agrees very closely with the doublet interval of 55 cm^{-1}, of the first excited $A^2\Pi$ state of MgCl Thus the lower state of the new doublet system was easily identified as the upper state of the main $A^2\Pi - X^2\Sigma$ system. All the observed features of the band system are in accordance with the predicted $B^2\Sigma - A^2\Pi$ The position of ν_{00} for the $B^2\Sigma$ state is obtained as 26520 4 + 21136.8 = 47657 2 cm^{-1} The approximate vibrational frequency of the upper state is estimated as 563 cm $^{-1}$ The lower state vibrational constants are the same as those of the main system Thus the analysis reported above shows conclusively that the emitter of the band system is diatomic MgCl

Isotope Effect The calculated isotopic separations of the less abundant molecule $MgCl^{37}$ according to the formula

$$\nu_i \quad \nu - (\rho - 1)[\omega_e'(v' + 1/2) \quad \omega_e''(v'' + 1/2)$$
$$(\rho^2 \quad 1)[x_e'\omega_e'(v' + 1/2)^2 - x_e''\omega_e''(v'' + 1/2)^2] + \ldots$$

for 0, 1 and 1, 0 bands are 5.03 and 6.5 wave numbers respectively While this separation is resolvable under dispersion used in the present work, the bands of 0,1 and 1.0 sequences are too weak for a detailed study of the chlorine isotopic effect. The weaker $MgCl^{37}$ heads for 0, 1 bands which are expected to occur on the shorter wave length side are overlapped by the shading of the stronger heads of the more abundant molecule $MgCl^{35}$. The bands of 1,0 sequence, though weak, are more favourable for the detection of the weaker $MgCl^{37}$ heads as they are expected to occur on longer wavelength side The P_1 and Q_1 heads of the 1, 0 band of the sub-system II were accompanied by the weaker isotopic heads. Although the observed separations of these two solitary heads agree fairly well with the calculated separations as can be seen from table IV, it may be remarked that the agreement tends to support the analysis and may not be taken as too significant or too substantial a support

TABLE IV

Isotopic Shifts

Band head	Observed Isotopic shift in cm^{-1}	Calculated Isotopic shifts in cm^{-1}
1,0 P_1	6	6 5
1,0 Q_1	5 6	6 5

ELECTRONIC CONFIGURATIONS AND ELECTRONIC STATES OF MgCl AND MgF

The electronic structures of the ground states of BeF, MgCl are expected to be similar as they contain the same number outer valence electrons The ground state of the diatomic molecules BeF and MgF is well known to be $^2\Sigma$ state Following Mullikan's notation the electron configuration of the ground state can be represented as

$$(z\sigma)^2\ (y\sigma)^2(W\pi)^4(x\sigma)\ldots{}^2\Sigma \qquad \ldots\quad (1)$$

The first excited $A^2\Pi_i$ state in BeF and MgF may be represented by the configuration

$$(z\sigma)^2\ (y\sigma)^2(W\pi)^3(x\sigma)^2\ \ldots\ {}^2\Pi_i \qquad \ldots\quad (2)$$

By analogy with BeF and MgF the $^2\Sigma$ and $^2\Pi_i$ terms arising from configurations from (1) and (2) account for the observed ground $X^2\Sigma$ and first excited $A^2\Pi$ states of MgCl The observed $B^2\Sigma$ state (upper state of the new doublet system) may be attributed to the configuration

$$(z\sigma)^2(y\sigma)^2(W\pi)^3(x\sigma)(v\pi)\ \ldots\ {}^2\Sigma \qquad \ldots\quad (3)$$

in which an electron from $(x\sigma)$ orbital goes to the $(v\pi)$ orbital A transition from the observed $B^2\Sigma$ state to the ground state cannot occur as configuration (3) involves a two electron jump from configuration (1) This might account for the fact that the $B^2\Sigma - X^2\Sigma$ transition was not experimentally observed

ACKNOWLEDGMENT

The authors wish to express their thanks of Prof K R Rao for his kind interest in this work One of the authors (V S N. Rao) is grateful to the C.S I.R. (New Delhi) for the financial assistance

REFERENCES

Harrington, R E , 1942, Dissertation (University of California).

Herzberg G 1953, Molecular spectra and Molecular structure I Spectra of Diatomic Molecules 2nd Edition (Van Nostrand Co . New York)

Jevons, W , 1932, Report on Band Spectra of Diatomic Molecules (Physical Society, London)

Morgan, F , 1936, *Physical Review*, **50**, 603

Parker, A E., 1935, *Physical Review*, **47**, 349

Quenbach, J , 1930, *Z Physik*, **60**. 109